OPTICAL, ADDITIONAL FILMS AND OPTICAL ELEMENTS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to optical, additional films suitably used, for example, in vacuum ultraviolet lithography, particularly, in F_2 laser lithography, optical elements in which the optical, additional film or films are added on a substrate, and optical apparatus using the optical element or elements.

The optical, additional films herein are such films as antireflection coatings, reflective coatings, or protective coatings, formed on surfaces of optical elements.

Related Background Art

Concerning the conventional i-line (wavelength 365 nm) and KrF laser (wavelength 248 nm) lithographies, glass materials for such optical elements as lenses, antireflection coating materials, environments, etc. that were applicable to optic systems of optical apparatus such as projection exposure apparatus, illumination apparatus, measuring apparatus, etc. used in such lithographies, were a direct extension of the conventional technologies and were able to be prepared by application of the conventional technologies.

As for the lithography in the vacuum ultraviolet

region, however, oxygen, water, etc. greatly absorbs light and it is thus necessary to keep an atmosphere under vacuum or to replace an atmosphere with gas such as nitrogen or helium.

In the ArF laser lithography at the wavelength of 193 nm, conventionally used silica and fluorite were applicable as glass materials and antireflection coating materials and it was also possible to select certain kinds of metal fluorides and oxides.

Silica (SiO_2) has been used heretofore as a material for optical elements for ArF laser. It was because silica (SiO_2) had the high transmittance of 90% for ArF excimer laser light and possessed the stable property against variation in temperature, humidity, and so on. However, the transmittance of silica (SiO_2) becomes extremely lowered for the F_2 laser light having the wavelength of 157 nm, and it is impossible to use it as an optical material.

On the other hand, in the F_2 laser lithography, only fluorite (CaF_2) is applicable as a glass material capable of sufficiently transmitting rays at the wavelength of 157 nm, which is hindrance to design of optical systems.

Further, the F_2 laser lithography also involves a problem concerning the optical, additional films such as the antireflection coatings or the like. In general the antireflection coatings are formed in multilayer

structure of combination of a material having a refractive index smaller than that of a material of a substrate with a material having a refractive index higher than that of the material of the substrate, thereby yielding a stronger antireflection effect than that of the antireflection coatings of monolayer structure.

However, no material with a refractive index higher than that of fluorite has been found yet as a material for antireflection coatings, so that magnesium fluoride (MgF_2) or lithium fluoride (LiF) with the refractive index lower than that of fluorite had to be used in monolayer structure in the F_2 laser lithography. Under such circumstances, there are desires for a material having a refractive index higher than that of fluorite and being capable of making the optical, additional films (antireflection coatings, reflective coatings, protective coatings) of multilayer structure in combination with MgF_2 or LiF, as a material for the optical, additional films for the F_2 laser lithography.

Japanese Patent Application Laid-Open No. 2000-89450 (Application No. 10-272570) suggests reticle materials applicable to the F_2 laser lithography. They are crystals of metal fluorides such as MgF_2, LiF, and CaF_2, which are used so that their crystallographic axis is oriented in a specific direction.

SUMMARY OF THE INVENTION

It is thus an object of the present invention to provide optical, additional films (antireflection coatings, reflective coatings, protective coatings, etc.) and optical elements applicable to the F_2 laser lithography.

The inventor conducted extensive and intensive research in order to solve the above problems and succeeded in developing effective element techniques for breakthrough improvement in performance of the optical systems of the optical apparatus such as the projection exposure apparatus, illumination apparatus, measurement apparatus, etc. used in the F_2 laser lithography and, in turn, for contribution to improvement in microprocessing and productivity of semiconductors and others.

One aspect of the present invention is a film comprising at least one layer of silica (SiO_2) containing fluorine (F).

In the film, preferably, a concentration of the fluorine in the layer or layers of silica is not less than 0.1 mol% (preferably, not less than 1 mol%) nor more than 10 mol%.

In the film, preferably, a refractive index of the layer or layers of silica for F_2 laser light is 1.60-1.80.

Preferably, the film comprises a layer a material

of which is selected from the group consisting of MgF_2, LiF, and Na_3AlF_6.

Another aspect of the invention is an optical element wherein the film as set forth is added on a surface thereof.

In the optical element, preferably, said optical element is comprised of fluorite.

In the optical element, preferably, said optical element is comprised of silica containing fluorine.

In the optical element, preferably, said film is an antireflection coating.

Another aspect of the invention is an optical apparatus for vacuum ultraviolet lithography, comprising the optical element as set forth.

Another aspect of the invention is a device fabrication method comprising a step of exposing a wafer to a device pattern by the optical apparatus as set forth, and a step of developing the wafer thus exposed.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view of a BO lens;

Figs. 2A and 2B are cross-sectional views of an 8-step BO lens;

Fig. 3 is a BO lens substrate before production of a BO lens;

Fig. 4 is a cross-sectional view of a BO lens and

three masks used in production of the BO lens;

Fig. 5 is a cross-sectional view of a BO lens with antireflection coatings of the present invention deposited on a front surface and a back surface;

Fig. 6 is a cross-sectional view of a lens with antireflection coatings of the present invention;

Fig. 7 is a view showing a mirror with a reflective film of the present invention on a surface; and

Fig. 8 is a drawing showing an embodiment of the optical apparatus according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

We propose here that silica containing fluorine (which will be also referred to hereinafter as "SiO_2:F") is used as a material for the optical films (additional films) (e.g., antireflection coatings, reflective coatings, or protective coatings) added on the substrate of the optical elements for the F_2 laser lithography.

The inventor succeeded in dramatically raising the transmittance of silica films for the F_2 laser light by adding a predetermined amount of fluorine to the silica films. A nondoped silica film 1 μm thick has the transmittance of not more than 10% for the F_2 laser light, whereas a silica film doped with about 1 mol% of fluorine has the transmittance raised to about 90% for

the F_2 laser light.

In general the materials of the optical elements for photolithography are required to have the transmittance of 90% or more for light of an objective wavelength. Silica films doped with fluorine have transmittances higher than it for the F_2 laser light and thus can be used as materials of the optical, additional films for the F_2 laser light.

The film of silica containing fluorine desirably has the transmittance of 90% or more for the F_2 laser light f 157 nm when the thickness thereof is 1 μm. Further, the transmittance is more desirably not less than 95% and most desirably not less than 99%.

The film of silica containing fluorine desirably has at least the refractive index higher than that of fluorite. This is because the refractive index (n) of fluorite is about 1.56 for the F_2 laser light having the wavelength of 157 nm and it becomes feasible to make a more efficient, optical, additional film, by employing a layered structure with either of MgF_2 (n = 1.47), LiF (n = 1.49), and Na_3AlF_6 (n = 1.48) having the refractive indices lower than that of fluorite.

More specifically, the refractive index of the SiO_2:F film is desirably 1.6 to 1.8.

As an example, the refractive index of the SiO_2:F film containing 1 mol% of fluorine for the F_2 laser light is 1.65 and this SiO_2:F film can be combined with

an LiF film or an MgF_2 film to obtain an efficient, optical, thin film (multilayer film) (reference is made to examples).

For using the silica containing fluorine (SiO_2:F) as an antireflection coating or a reflective coating for the F_2 laser lithography, a content of fluorine in the silica film is desirably 0.1 mol% to 10 mol%.

When the concentration of fluorine is not less than 0.1 mol%, the silica film containing fluorine has a practically allowable transmittance for the F_2 laser light. When the fluorine concentration is not more than 10 mol%, it is possible to maintain stable, optical characteristics (refractive index, transmittance, etc.) and film properties.

The fluorine content is more desirably in the range of not less than 1 mol% nor more than 10 mol%.

In the fluorine-containing silica as a material for the optical, additional films (antireflection coatings, reflective coatings, protective coatings) or as a material for the optical elements, fluorine is desirably present everywhere in a constant concentration. If fluorine is scattered in a constant concentration in in-plane and depth directions, there will occur no fluctuations in the optical characteristics and film properties including the refractive index and the transmittance, depending upon locations.

A method of forming the fluorine-containing silica film can be selected arbitrarily from well-known methods that can form the silica film and make the silica film contain fluorine in the aforementioned concentration range.

For example, such conventional methods include chemical vapor deposition (CVD), sputter deposition, ion beam sputtering deposition, reactive sputtering deposition, electron beam evaporation, and so on.

When the fluorine-containing silica (SiO_2:F) film is formed by these methods, it is important to avoid dispersion of fluorine concentration (in the in-plane and depth directions) in the film.

For example, when the film is formed by the reactive sputtering deposition method, a sputter target is desirably silica (SiO_2) or fluorine-containing silica (SiO_2:F). Sputter gas is desirably inert gas (Ar, Ne, He, Kr, or the like) and reaction gas desirably fluorine gas (F_2).

When the film is formed by sputter deposition, it is desirable to preliminarily prepare a target of silica doped with fluorine (SiO_2:F) by another method, use inert gas (Ar, Ne, He, Kr, or the like) as the sputter gas, and implement sputtering of the target.

In these film-forming methods making use of the sputtering phenomenon, the composition of the deposited film often disagrees with the composition of the target

because of influence of selective sputtering or the like, and it is thus desirable to supplement fluorine so as to obtain the film in the objective fluorine concentration.

One form of the optical, additional films according to the present invention is a multilayer film consisting of a stack of alternate films being a combination of the fluorine-containing silica (SiO_2:F) film with a metal fluoride, specifically, either of MgF_2, LiF, Na_3AlF_6, CaF_2, LaF_2, BaF_2, SrF, and so on.

Particularly, the optical, additional films for the F_2 laser lithography are more desirably of the stack structure of SiO_2:F and LiF, Na_3AlF_6, or CaF_2 films.

Examples of the stack structure of the optical, additional films for the F_2 laser lithography will be presented below. When the films are formed in two-layer structure, desirable structures are MgF_2 (265 Å)/SiO_2:F (238 Å)/fluorite (optical element), LiF (265 Å)/SiO_2:F (238 Å)/fluorite (optical element), and Na_3AlF_6 (265 Å)/SiO_2:F (238 Å)/fluorite (optical element). The thickness of each layer indicated by (...Å) was determined according to the condition for interference film at 157 nm (the wavelength of F_2 laser light).

When the films are formed in four-layer structure, desirable structures are MgF_2 (434 Å)/SiO_2:F (238 Å)/MgF_2 (434 Å)/SiO_2:F (238 Å)/fluorite (optical

element), LiF (434 Å)/SiO_2:F (238 Å)/LiF (434 Å)/SiO_2:F (238 Å)/fluorite (optical element), and Na_3AlF_6 (434 Å)/SiO_2:F (238 Å)/Na_3AlF_6 (434 Å)/SiO_2:F (238 Å)/fluorite (optical element). The thickness of each layer was also determined according to the condition for interference film at 157 nm (the wavelength of F_2 laser light).

The optical, additional films of the present invention are not limited to be added only on the surfaces of lenses, but can also be added on surfaces of diffraction gratings, mirrors, and filters, whereby a remarkable effect can be expected on improvement in diffraction efficiency and on increase of reflectance.

These optical elements (diffraction gratings, lenses, mirrors, filters) with the optical, additional films are also one aspect of the present invention.

The optical apparatus using these optical elements as components are also one aspect of the present invention. The optical apparatus herein embraces the projection exposure apparatus, illumination apparatus, measurement apparatus, and so on used in the F_2 laser lithography.

The present invention will be described hereinafter in further detail with examples thereof.

(Example 1)

A circular BO (Binary Optics) lens having the diameter of 20 mm was made.

The BO lens herein is a kind of diffraction grating and the diffraction grating is normally used as a spectroscopic element of a spectroscope in the optical apparatus for fabrication of semiconductors. The BO lens has a stepwise diffraction grating and is expected to be applied to optical systems using ultraviolet light because of its potential of achromatism and aspheric effect.

The present BO lens is designed to work at the wavelength of the F_2 laser light of 157 nm and has about 1800 rings. Each ring has a stepwise structure of eight steps.

Fig. 1 and Figs. 2A and 2B are schematic views of the BO lens and the stepwise structure of the rings thereof, respectively. The outermost ring has such designed values that the width of each step is 0.35 µm, the height of each step 0.04 µm, and the width and height of the ring are 2.8 µm and 0.28 µm, respectively. Fig. 2A is a partial magnification of Fig. 2B.

This BO lens was fabricated in such a way that a substrate 1 of fluorite having the diameter of 2 inches and the thickness of 4 mm as shown in Fig. 3 was prepared, patterns of chromium masks (11 to 13) having different intervals were successively printed as reduced images in respective, negative photoresists coated on the substrate 1, using a stepper for

KrF (λ = 248 nm), each photoresist was developed after printed to obtain a resist pattern, and the substrate 1 was etched by a dry etching method using the resultant resist patterns as masks. Gas for the dry etching was a mixture of argon and hydrogen.

Fig. 4 is an explanatory drawing simultaneously showing the three masks (11 to 13) successively used for the fabrication of the present BO lens, together with the lens. The above process was repeated three times while changing the masks, thereby making the BO lens of the stepwise structure with rings each consisting of eight steps.

In the present invention, antireflection coatings consisting of alternate layers of SiO_2:F layers were laid on the front surface and on the back surface of the BO element fabricated as described above (Fig. 5).

The coatings were formed by the reactive sputtering deposition method. The sputtering target was a synthetic quartz sheet. The film forming system was a sputtering deposition system of RF type (model SBR-110 available from Ulvac Inc.).

The sputtering deposition was carried out under the conditions of Table 1.

In order to evaluate the physical properties of the SiO_2:F films of the present invention, a substrate of flat plate shape (hereinafter referred to as a test sample) made of the same material as the BO element was

also introduced into the deposition chamber and subjected to deposition at the same time.

TABLE 1

deposition conditions	Values
sputtering target	SiO_2
pressure in deposition chamber	4 Pa
substrate temperature (temperature of BO element)	22° C
sputter gas and reaction gas	10vol%F_2-containing Ar gas, 20 sccm
deposition time	7.6 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

Evaluation was made for the physical properties of the SiO_2:F films thus deposited on the BO element. This evaluation for the physical properties was conducted with the test sample.

Cross sections of the test sample were observed with a scanning electron microscope and it was found from the observation that the thickness of the SiO_2:F films was 238 Å.

The concentration of fluorine (F) in the SiO_2:F films was evaluated by Raman spectroscopy, and the fluorine concentration was approximately 1 mol%.

Further, a depth profile analysis by SIMS (Secondary ion mass spectrometry) was performed to obtain a profile of F in the depth direction in the SiO_2:F films, and it was verified that F was distributed in a constant concentration in the SiO_2:F films.

The refractive index of the SiO_2:F films was measured at the wavelengths of 200 to 300 nm with an ellipsometer and the refractive index was approximately 1.65 for the F_2 laser light (at the wavelength of 157 nm) from extrapolation of the measurement results.

After completion of the deposition of the SiO_2:F films, lithium fluoride (LiF) was then deposited subsequently without taking the substrate out of the deposition system. The deposition conditions are presented in Table 2.

TABLE 2

deposition conditions	Values
sputtering target	LiF
pressure in deposition chamber	2 Pa
substrate temperature (temperature of BO element)	22°C
sputter gas and reaction gas	10vol%F_2-containing Ar gas, 10 sccm
deposition time	9.7 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

The physical properties of the LiF films thus deposited were also evaluated with the test sample.

Cross sections of the test sample were observed with the scanning electron microscope and the thickness of the LiF film was 263 Å.

The diffraction efficiency of this BO element was measured with a diffraction efficiency measuring system and the BO element demonstrated an improvement of 14% on average in the diffraction efficiency, as compared with elements without the antireflection coatings.

(Example 2)

Antireflection coatings 5 having the structure of "MgF_2/SiO_2:F/lens surface" were deposited on surfaces of fluorite lens 2 for the F_2 laser light having the wavelength of 157 nm (Fig. 6). The lens 2 is a lens for the F_2 lithography and has the lens diameter of 100 mm and the thickness of 10 mm in the thickest portion.

In the present example, the SiO_2:F films were deposited in the thickness of 238 Å by sputtering a target of fluorine-containing silica by RF sputtering. The deposition conditions of the SiO_2:F films in the present example are presented in Table 3.

TABLE 3

deposition conditions	Values
sputtering target	SiO_2:F
pressure in deposition chamber	2 Pa
substrate temperature (temperature of lens)	22° C
sputter gas and reaction gas	Ar gas, 10 sccm
deposition time	6.9 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

The concentration of fluorine (F) in the SiO_2:F films was evaluated by Raman spectroscopy, and the fluorine concentration was approximately 1 mol%. Further, the depth profile analysis by SIMS (Secondary ion mass spectrometry) was performed to obtain a profile of fluorine in the depth direction in the SiO_2:F films, and it was verified that fluorine was distributed in a constant concentration in the SiO_2:F films.

The refractive index of the SiO_2:F films was measured at the wavelengths of 200 to 300 nm with the ellipsometer and the refractive index was approximately 1.65 at the wavelength of 157 nm of the F_2 laser light from extrapolation of the measurement results.

Further, magnesium fluoride (MgF_2) films were deposited as upper layers in the thickness of 263 Å by similar means. The deposition conditions at that time are presented in Table 4.

TABLE 4

deposition conditions	Values
sputtering target	MgF_2
pressure in deposition chamber	2 Pa
substrate temperature (temperature of lens)	22° C
sputter gas and reaction gas	Ar gas, 10 sccm
deposition time	19 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

Similarly, an antireflection coating 5 of two layers was also laid on the back surface of the lens 2.

The transmittance of the complete lens was measured for the F_2 laser light of 157 nm and the transmittance was improved by about 8% in the central part.

(Example 3)

A film having the structure of "MgF_2/SiO_2:F/mirror surface" was laid as a reflective coating 6 on a surface of a reflecting mirror used in an optical path

of a spectrophotometer (Fig. 7).

A fluorine-containing silica (SiO_2:F) film was deposited as a reflective coating 6 in the thickness of 265 Å on an aluminum (Al) deposited film 4 formed on a glass substrate 3, using the sputtering system similar to that used in Example 1. The thickness (265 Å) of this film 6 was determined from the condition of the interference film for rays of 157 nm.

The deposition conditions of the SiO_2:F film are the same as in Example 1.

The deposition conditions of the MgF_2 film are presented in Table 5.

TABLE 5

deposition conditions	Values
sputtering target	MgF_2
pressure in deposition chamber	2 Pa
substrate temperature (temperature of reflecting mirror)	22° C
sputter gas and reaction gas	10vol%F_2-containing Ar gas, 10 sccm
deposition time	11.1 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

The reflectance of the reflection-enhanced mirror (Fig. 7) obtained in this way was measured and it was verified that the reflectance was enhanced by 7% at the angle of incidence of 45° for the F_2 laser light.

There was no choice but to use an Al film in an exposed state for the conventional mirrors for the F_2 laser light. The reason was that if an optical, additional film was laid on the surface the reflectance of the mirror was heavily lowered. For this reason, lives of the conventional mirrors were short and the mirrors had to be replaced frequently.

However, it became feasible to extend the life of the mirror to double or more those of the conventional mirrors, by laying the optical, additional film of the present invention on the surface of the Al mirror.

(Example 4)

The lens of the same shape as in Example 3 was made of a material of silica containing 4 mol% of fluorine (SiO_2:F). Further, antireflection coatings 5 having the stack structure of four layers of "LiF/SiO_2:F/LiF/SiO_2:F/lens surface" were formed on the lens surfaces (on the front surface and on the back surface). The deposition conditions of SiO_2:F and LiF were the same as in Example 1.

The concentration of fluorine (F) in the SiO_2:F films was evaluated by Raman spectroscopy, and the fluorine concentration was approximately 1 mol%.

Further, the depth profile analysis by SIMS (Secondary ion mass spectrometry) was performed to obtain a profile of fluorine in the depth direction in the SiO_2:F films, and it was verified that fluorine was distributed in a constant concentration in the SiO_2:F films.

The refractive index of the SiO_2:F films was also measured at the wavelengths of 200 to 300 nm with the ellipsometer and the refractive index was approximately 1.65 at the wavelength of 157 nm of the F_2 laser light from extrapolation of the measurement results.

The transmittance of the lens of the present example was measured for the F_2 laser light and it was verified therefrom that the transmittance was improved by about 8%.

(Example 5)

The optical, additional films were made by resistance heating evaporation, instead of the film forming methods of the fluorine-containing silica (SiO_2:F) films, magnesium fluoride (MgF_2) films, and lithium fluoride (LiF) films in Examples 1, 2, and 3. The present example also confirmed the improvement in the diffraction efficiency of the BO lens, the improvement in the transmittance of the lens, and the enhancement of reflectance of the mirror as in Examples 1, 2, and 3.

(Example 6)

The antireflection coatings as made in Example 5 were laid on surfaces of optical elements (lenses, mirrors, diffraction gratings) used in the optical systems of the projection exposure apparatus (steppers or scanners) for fabrication of semiconductors using the F_2 laser for printing. As a result, the lenses demonstrated the increase of about 8% in the transmittance, the mirrors the increase of about 8% in the reflectance, and the diffraction gratings the increase of about 15% in the diffraction efficiency. Fig. 8 is a schematic view of this projection exposure apparatus. The optical, additional films of the present invention are used in the optical elements of its illumination system and/or in the optical elements of its projection system and/or in the optical elements of masks and the like.

The transmittance of the entire projection exposure apparatus was improved for the F_2 laser light by virtue of the effect of the optical, additional films laid on these optical elements and it thus became feasible to fabricate the semiconductor devices in higher density than before.